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Review

Equations of State of Atoms for the Thomas-Fermi Theory (Applications for Atoms under a High Pressure)

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The most simple model of atoms is a spherical atom in which the charge due to electrons is uniformly distributed. In the second model, the potential in an atom is expressed, instead of a uniform distribution, as a function of distance from the central nucleus concerned. In this case, by introducing a non-dimensional statistical potential, quantitative estimates of atomic behavior can be approximately made. This is called the Thomas-Fermi (TF) method. This method is much simpler than the self-consistent field method, but in some cases, at least for the ground state of atoms, the TF method is useful without critical loss of accuracy. The principle of the TF method is reviewed as well as applications of the method for atoms compressed under a high pressure.

I. INTRODUCTION

The equation of state of material is, in general, expressed in terms of pressure P , volume v and temperature T , and thus is treated from the macroscopic point of view. However, starting from the total energy (kinetic energy+potential energy) of electrons contained in the atom in question, it is possible to obtain the equation of atomic state and to applicate to the macroscopic state of the many-atom system.

There are several ways to obtain the energy of atomic electrons. The self-consistent field theory of Hartree¹⁾ and Hartree-Fock²⁾ provides the most reliable solutions for the atomic behavior. But, because of complexity in calculations, this method is not always proper for investigations of the overall atomic behavior.

By introducing a statistical potential, investigations of atomic state, at least for the ground state configuration, can be made much easier than in the self-consistent field method. This is the TF method,^{3~5)} where the potential is given as a function of distance r from the central nucleus. Since the equation of state in the TF method is subject only to atomic number and its radius, it should give informations on the energy of electrons in the atom of which boundary is altered by any external condition. This fact indicates that the TF method can be used to find atomic behavior compressed under a high pressure.

In the present article, the equation of state of atoms by means of the TF method is presented. For simplicity, temperature T is considered to be constant. Comparisons of the theoretical result obtained by the TF method to some experimental data on the compressibility of atoms are also made to check the utility of this method.

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II. THOMAS-FERMI METHOD

In the TF method, the atomic model is assumed to be as follows:

- (1) Atoms are spherical.
- (2) The potential in atoms is spherically symmetry and is almost constant in the range much larger compared to the electron wave length.
- (3) The exchange interaction is neglected.
- (4) The whole electron system is in the lowest energy state.

We also introduce the following two boundary conditions:

- (a) The electric potential near the nucleus is approximated by Ze/r , where Ze is the nuclear charge and r is the distance from the nucleus.
- (b) The total charge of electrons in the atom is $-Ze$, i.e., the atom is electrically neutral.

Suppose that the total potential energy of electrons is $-eV(r)$, including mutual interactions with the nucleus and other electrons contained in the atom. If the total energy of electrons in this field is represented by $-eE$, we have

$$\frac{p^2}{2m} - eV(r) = -eE, \quad (1)$$

where p is the electron momentum, m is the electron mass.

Taking into consideration the assumption (2), we introduce the Fermi-Dirac statistics. When the absolute temperature T is zero, the number of states which fall into the momentum range between p and $p+dp$ is $(8\pi/h^3)p^2 dp$ per unit volume, where spin is taken into account and h is the Planck constant. If the maximum momentum of electrons corresponding to the maximum energy is assigned as p_{\max} , the integration in the momentum space from zero to p_{\max} gives the state density in the ordinary Cartesian coordinates, which is

$$\int_0^{p_{\max}} \frac{8\pi}{h^3} p^2 dp = \frac{8\pi p_{\max}^3}{3h^3}, \quad (2)$$

where $p_{\max} = [-2me(E_0 - V)]^{1/2}$. The charge density of electrons is given by Eq. (2) multiplied by $-e$,

$$\rho = -\frac{8\pi e}{3h^3} [-2me(E_0 - V)]^{3/2}. \quad (3)$$

Using the Poisson equation

$$\nabla^2 V(r) = -4\pi\rho, \quad (4)$$

the resulting equation is

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dV}{dr} \right) = \frac{32\pi^2 e}{3h^3} [2me(V - E_0)]^{3/2}. \quad (5)$$

Let introduce new variables here as given in the following relations

$$\left. \begin{aligned} r &= \mu x, \\ \mu &= a_0 \left(\frac{9\pi^2}{128Z} \right)^{1/3}, \\ V - E_0 &= \frac{r\phi}{x}, \quad r = \frac{Ze}{\mu}, \end{aligned} \right\} \quad (6)$$

where a_0 is the Bohr radius. From Eq. (6), we get

$$(V - E_0)r = Ze\phi. \quad (7)$$

The above equation indicates that the quantity $Ze\phi$ is of the nature of an effective nuclear charge, which is smaller than Ze due to the shielding effect of electrons surrounding the nucleus. From Eq. (7), it is evident that $Ze\phi/r$ is the effective potential in the atom. In other words, ϕ is a non-dimensional parameter which gives the effective potential in the atom.

According to the boundary condition (a), the potential near the nucleus is Ze/r , so that as r goes to zero, $Ze\phi$ approaches Ze . This leads to the new boundary condition

$$\phi(0) = 1. \quad (8)$$

By the boundary condition (b), the atom in question is electrically neutral. Thus, the electric field at the boundary of the spherical cell must be zero. From Eq. (7)

$$\left(\frac{dV}{dr} \right)_{r=r_0} = -\frac{Ze\phi}{r_0^2} + \frac{Ze}{r_0} \left(\frac{d\phi}{dr} \right)_{r=r_0} = 0. \quad (9)$$

In terms of the new variables, Eq. (9) becomes

$$\left(\frac{d\phi}{dx} \right)_{x=X} = \frac{\phi(X)}{X}, \quad (10)$$

where $r_0 = \mu X$. Eq. (10) is the new boundary condition corresponding to the second boundary condition (b).

At this stage, let get back to the Poisson equation, which can be rewritten in terms of the new variables. This gives

$$\frac{d^2\phi}{dx^2} = \frac{\mu^2}{\gamma} \frac{32\pi^2 e}{3h^3} (2me\gamma)^{3/2} \frac{\phi^{3/2}}{x^{1/2}}. \quad (11)$$

The above equation becomes a simple second order derivative equation by eliminating γ and μ , which is

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}}. \quad (12)$$

This is called the TF equation. The boundary conditions imposed on Eq. (12) are of course Eqs. (8) and (10). The solution of Eq. (12) can be obtained by numerical

calculations. The typical solution obtained by Slater and Krutter⁵⁾ is shown in Fig. 1. If the initial slope of the TF parameter, $\phi'(0)$, is equal to -1.58808 , ϕ approaches asymptotically to the x axis as x goes to infinite. This means that, for $\phi'(0) = -1.58808$, the atomic boundary is at $x = \infty$ (free atom). When $\phi'(0) > -1.58808$, ϕ has a minimum value at a certain value of x . In this case, as evident from Eq. (10), the tangent to the curve ϕ at $x = X$ should pass through the origin of the coordinate.

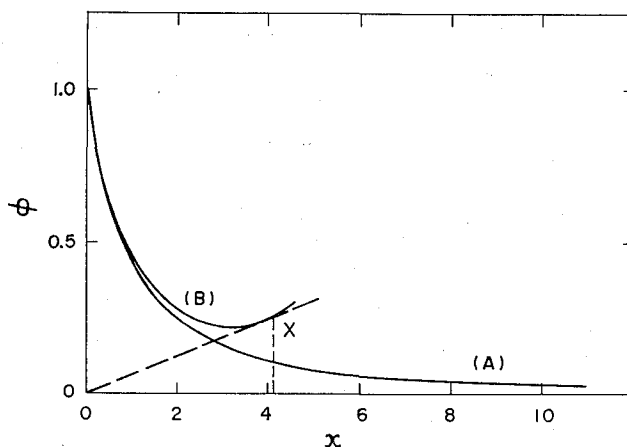


Fig. 1. The TF function $\phi(x)$ versus the distance from the center of the atom, x . (A) $\phi'(0) = -1.58808$ (free atoms), (B) $\phi'(0) > -1.58808$ (atoms with the finite boundary X).

III. KINETIC ENERGY OF ELECTRONS IN AN ATOM

III.1. When the Atomic Boundary is at $x = \infty$

The maximum kinetic energy of electrons in a free atom is $p_{\max}^2/2m$, which is equal to the Fermi energy E_F , i.e.,

$$\frac{p_{\max}^2}{2m} = e(V - E_0) = E_F. \quad (13)$$

By substituting the relation $(V - E_0) = Ze\phi/\mu x$, E_F becomes

$$E_F = \frac{Ze^2\phi}{\mu x}. \quad (14)$$

The total kinetic energy, E_{kin} , of the whole system is

$$E_{\text{kin}} = \int_0^\infty N\langle E \rangle 4\pi r^2 dr, \quad (15)$$

where $\langle E \rangle$ is the average kinetic energy of electrons and N is the number of electrons. As suggested in Sec. II, the potential in the atom is almost constant in much larger range compared to the electron wave length. Therefore, if the Fermi-Dirac

statistics for $T=0$ are approximately satisfied, the average energy of electrons becomes

$$\langle E \rangle = \frac{8\pi v}{5h^3 N} (2m)^{3/2} E_F^{5/2}, \quad (16)$$

where v is the volume of the atom. Then, from Eqs. (15) and (16), E_{kin} is

$$E_{\text{kin}} = \frac{8\pi}{5h^3} (2m)^{3/2} \int_0^\infty E_F^{5/2} 4\pi r^2 dr. \quad (17)$$

Substituting Eq. (14) in Eq. (17), we get

$$E_{\text{kin}} = \frac{32 \times 3^{1/3} \pi^{4/3} m e^4 Z^{1/3}}{5 \times 2^{2/3} h^2} \int_0^\infty \frac{\phi^{5/2}}{x^{1/2}} dx, \quad (18)$$

where r is converted to x . Eq. (18) can be calculated by means of integration by parts and also by using Eq. (12). The result is

$$E_{\text{kin}} = -\frac{3}{7} Z e r \phi'(0). \quad (19)$$

III.2. When the Atom has the Finite Radius X

In this case, the upper limit of integration in Eq. (18) should be replaced by X in the calculation of E_{kin} . Carrying out the integration over x , the final result of E_{kin} is

$$E_{\text{kin}} = -\frac{3}{7} Z e r \left[\phi'(0) - \frac{4}{5} X^{1/2} \phi^{5/2}(X) \right]. \quad (20)$$

IV. POTENTIAL ENERGY OF ELECTRONS IN AN ATOM

IV.1. When the Atomic Boundary is at $x=\infty$

The potential energy per atom is, in general, given by the following equation

$$E_{\text{pot}} = \frac{1}{2} \int \rho V dv + \frac{1}{2} Z e V_0, \quad (21)$$

where V is the whole potential and V_0 is the potential at the nucleus due to electrons. The quantity ρ is the charge density due to electrons, which is given by $-ne$ (n is the electron density). Since the whole potential V is $Ze\phi/r$ and the potential due to ρ near the nucleus is $-ne/r$, Eq. (21) becomes

$$\begin{aligned} E_{\text{pot}} &= -\frac{1}{2} \int \frac{Ze\phi}{r} n e dv - \frac{1}{2} Z e \int \frac{ne}{r} dv \\ &= -\frac{1}{2} \int \frac{Ze^2}{r} (1+\phi) n 4\pi r^2 dr. \end{aligned} \quad (22)$$

The electron density n is related to E_F by the well known equation,

$E_F = (\hbar^2/2m)(3n/8\pi)^{2/3}$, and hence from Eq. (14) we get

$$n = \frac{8\pi}{3} \left(\frac{2mZ}{r} \right)^{3/2} \left(\frac{e}{\hbar} \right)^3 \phi^{3/2}. \quad (23)$$

Substituting Eq. (23) in Eq. (22), E_{pot} is

$$E_{\text{pot}} = -\frac{8 \times 6^{1/3} \pi^4 Z^{7/3} m e^4}{3 \hbar^2} \int_0^\infty \frac{\phi^{3/2} + \phi^{5/2}}{x^{1/2}} dx. \quad (24)$$

By integrating the above equation over x , the final result of E_{pot} is

$$E_{\text{pot}} = \frac{6}{7} Z e r \phi'(0). \quad (25)$$

IV.2. When the Atom has the Finite Radius X

As for the case of Sec. III.2, the upper limit of integration in Eq. (24) is replaced by the finite value X . By similar calculations to those for the kinetic energy, E_{pot} of the atom with the finite boundary is obtained,

$$E_{\text{pot}} = \frac{6}{7} Z e r \left[\phi'(0) - \frac{1}{3} X^{1/2} \phi^{5/2}(X) - \frac{7}{12} \frac{\phi(X)}{X} \right]. \quad (26)$$

V. EQUATIONS OF STATE OF ATOMS

As described in the preceding section, E_{kin} and E_{pot} of electrons in the atom are determined as a function of TF function $\phi(x)$. For arbitrary X , E_{kin} , and E_{pot} are related through the virial theorem,⁶⁾ which takes the form

$$E_{\text{kin}} + \frac{1}{2} E_{\text{pot}} = \frac{3}{2} P v, \quad (27)$$

where P denotes the pressure and v is the volume. Substituting Eqs. (20) and (26) in Eq. (27), the equation of state can be obtained as

$$P v = Z e r \left[\frac{2}{15} X^{1/2} \phi^{5/2}(X) - \frac{1}{6} \frac{\phi(X)}{X} \right]. \quad (28)$$

The problem we have to consider at this stage is how to determine the TF function $\phi(x)$. There are several methods⁷⁻¹¹⁾ to get $\phi(x)$. As an example, the method by March¹²⁾ which can be applied for atoms under an ultra-high pressure is presented here.

Supposing the atomic radius X is small enough, the solution $\phi(x)$ is expanded in a Taylor series around the boundary point X . Then we have

$$\left. \begin{aligned} \phi(x) &= \phi(X) + \sum_{n=1}^{\infty} t_n (X-x)^n \\ t_n &= \frac{(-1)^n}{n!} \phi^{(n)}(X) \end{aligned} \right\} \quad (29)$$

where $\phi^{(n)}(x)$ is the n th derivative of $\phi(x)$. For convenience, we introduce a parameter a defined by

$$\phi'(X) = \frac{\phi(X)}{X} = a^2. \quad (30)$$

Then the coefficients of the Taylor series are expressed in terms of X and a . With the coefficients, the Taylor series of $\phi(x)$ is

$$\begin{aligned} \phi(x) = & \phi(X) - a^2(X-x) + \frac{a^3}{2}X(X-x)^2 \\ & - \frac{a^3}{6}(X-x)^3 + \frac{a^4}{16}X(X-x)^4 - \frac{a^4}{80}(X-x)^5 + \dots \end{aligned} \quad (31)$$

Determinations of a as a function of X can be achieved by imposing the boundary condition $\phi(0)=1$

$$\begin{aligned} \phi(0) &= 1 \\ &= \frac{1}{3}a^3X^3 + \frac{1}{20}a^4X^5 + \dots \end{aligned} \quad (32)$$

Thus,

$$a \approx \frac{3^{1/3}}{X} \left(1 - \frac{1}{20}aX^2 + \dots \right). \quad (33)$$

From Eqs. (30) and (33), $\phi(X)$ is approximately given by

$$\phi(X) \approx \frac{3^{2/3}}{X} \left(1 - \frac{3^{1/3}}{10}X + \dots \right). \quad (34)$$

Substituting this equation in Eq. (28) and using the relation $v=(4\pi/3)(\mu X)^3$, the equation of state in terms of P and v is obtained,

$$\begin{aligned} PZ^{-10/3} &= \frac{7}{60} \left(\frac{3}{8\pi} \right)^{2/3} \frac{h^2}{m} (Zv)^{-5/3} \\ &\times \left[1 - \frac{20}{7} \frac{\pi m e^2}{h} (4Zv)^{1/3} + \dots \right]. \end{aligned} \quad (35)$$

In order to check the utility of the TF method for the atom under a high pressure, comparisons of the calculated results by this method with some experimental data are made. Altshuler *et al.*¹³⁾ proposed a method for determination of pressures and densities of shock compressions. The dynamic compressibility of ²⁹Cu, ³⁰Zn, ⁴⁷Ag, ⁴⁸Cd, ⁵⁰Sn, ⁷⁹Au, ⁸²Pb, and ⁸³Bi were measured in the pressure range of 0.4~4 Mbar. The largest change in density observed was about 2.28 for bismuth. In Fig. 2, the experimental values by Altshuler *et al.* for ³⁰Zn, ⁵⁰Sn, ⁸²Pb, and ⁸³Bi are shown with the theoretical values calculated by Latter *et al.*^{8,9)} by means of the TF method.

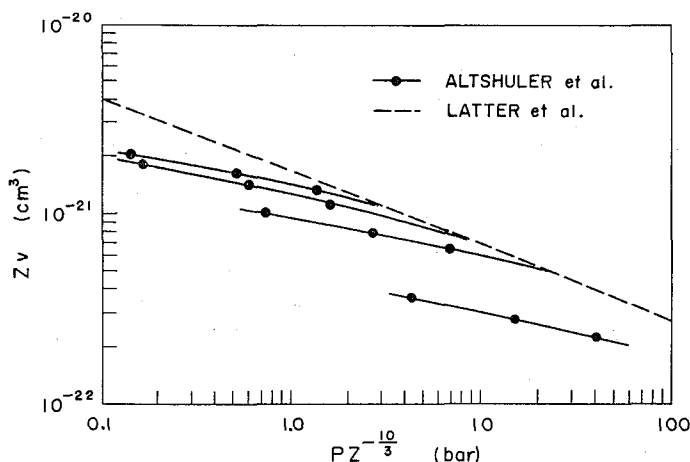


Fig. 2. Volume changes of various elements by shock compressions (Ref. 13) and the TF function calculated by Latter *et al.* (Refs. 8, 9).

By comparing both values, theoretical and experimental, and taking into consideration large errors which are unavoidable in a high-pressure experiment, the approximation by the TF method can be considered as a good approximation for elements of $Z > 50$ and for pressures over several Mbar. However, for light elements compressed in the pressure range of less than Mbar, the TF method is not useful anymore.

As described in the present article, the atomic radius X is the only important physical parameter in the TF method. It should be noted that in the TF method the same potential is used for all configurations of the atom. It is evident, therefore, that the error introduced in this approximation grows with increasing excitation of the atom. For excited atomic states, the TF method should be modified by means of the perturbation corrections to the energies and wave functions. This notwithstanding, the TF method may give some important informations on atomic states. Applications for the atom compressed by a high pressure is a good example.

In the TF method, the exchange interactions are not taken into account. Dirac¹⁴⁾ introduced the exchange factor in the TF equation. This is called the Thomas-Fermi-Dirac equation, which is much better approximation for atoms under a high pressure. Reviews on the TFD method will appear elsewhere.

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